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DETERMINATION OF RETAINED GAS IN IRRADIATED FUEL SAMPLES

M. Mogensen

Paper presented at the EEC Hot Laboratory Committee Meeting,
Mol, Belgium, 10-11 June 1982

Abstract. Full cross section samples from water reactor fuel pins are oxidized in molten NaNO_3 containing about 10% NaOH and 5% Na_2O_2 . During this oxidation the fission gases Kr and Xe are released. The gas volume is measured, and the gas is analysed by mass spectrometry.

The generated amount of gas in the samples analysed is calculated from measured burn-up, from measured Xe and Kr isotope ratios and from fission yields of stable Xe and Kr isotopes with low neutron capture cross sections. From the fission gas generated and measured amount of gas retained, the gas retention and release percentage can be found.

(Continue on next page)

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Examples of results are reported. Retained gas plus released gas (measured by puncturing) and the calculated gas generation agreed within 6 percent.

INIS descriptors: FISSION YIELD; FISSION PRODUCTS; FISSION PRODUCT RELEASE; FUEL PINS; ISOTOPE RATIO; KRYPTON; KRYPTON ISOTOPES; MASS SPECTROSCOPY; MEASURING METHODS; MOLTEN SALTS; OXIDATION; POST-IRRADIATION EXAMINATION; RADIATION CHEMISTRY; SPENT FUELS; URANIUM DIOXIDE; XENON; XENON ISOTOPES

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1. INTRODUCTION

To determine the degree of gas retention for a given irradiated reactor fuel sample, two quantities are needed: 1) the actual gas content of the sample which can be measured and 2) the quantity of gas contained in the fuel in case no release had occurred. The last quantity is in the present text called the Fission Gas Generation (FGG), and it can of course only be measured in case of no release, hence generally it must be calculated.

Different problems are involved in the procurement of these two quantities.

Regarding the first mentioned, most known techniques for determination of retained gas is based on dissolution of the fuel by nitric acid (Ref. 1-3) or by molten KHSO_4 (Ref. 4). These methods involves complicating steps of purification and/or separation after fuel dissolution before the amount of retained gas can be measured.

The second quantity, FGG, is usually calculated from burn-up and fission yields. The problem here is that the literature gives a very varying information of Xe and Kr fission yields. According to Ref. 5 the fission yield of Xe + Kr is 30%, and Ref. 6 gives a theoretical maximum of 31% for Xe + Kr. Ref. 7 reports for fuel irradiated by thermal neutrons two sets of yields, 21.6% and 26.1% for Xe and 3.5% and 3.7% for Kr in case of low (10 W/g UO_2) and high (100 W/g UO_2) rated fuel respectively. Ref. 8 gives a Xe yield of 22.3% without stating the Kr yield.

The present paper describes a new simple technique for measuring the retained fission gas and an accurate method for calculating the fission gas generated. This FGG calculation is based on post irradiation measurements performed on the relevant fuel.

2. EXPERIMENTAL TECHNIQUE

The oxidation of the UO_2 in the molten salts was carried out in a cylindrical stainless steel (AISI 316) container. This container was placed inside a vacuum unit (also made of stainless steel) in a vertical tube furnace, Adamel T5, as sketched in Fig. 1.

An extra insulation of 100 mm mineral wool was put onto the furnace, so that the surface temperature was kept below 50°C , and a removable temperature screening was placed over the furnace in order to protect the master slides manipulators.

Chemicals, NaNO_3 , NaOH and Na_2O_2 , used were analytical grade products from Merck. Oxidation experiments were performed on unirradiated and irradiated UO_2 . The unirradiated UO_2 was in the form of sintered pellets 12.5 mm diameter and weighed about 16 g. The pellets were put into Zircaloy cladding in order to obtain the same reaction condition as for the irradiated samples.

As part of the RISØ Fission Gas Project (Ref. 12) irradiated samples with burn-up from 2.4% to 4.5% were oxidized with the intention of determining the gas retention. The specimens were from a Danish fuel assembly irradiated in the OECD Halden Reactor. The burn-up was measured by Cs137 gamma counting, which was calibrated by isotopic analysis of Nd146 . Burn-up distribution on U235 , Pu239 and Pu241 was also established by isotopic analysis (Ref. 13).

The fuel samples were weighed including cladding. The cladding dimensions were known with an accuracy which allowed a calculation of the cladding weight within ± 0.1 g. The weight of the fuel was between 15 and 20 g giving a relative accuracy of approximately 0.5% and always better than 1%, the weighing uncertainty of ± 10 mg being negligible.

The furnace temperature was in all cases 500°C , and the oxidation time was 10 h in case nothing else is stated. The gas was extracted by means of a Hg-diffusion pump and a Toepler pump, and the gas

volume measured. The chemical as well as the isotope composition of the gas was analysed by a Varian CH5D mass spectrometer equipped with a gas inlet system.

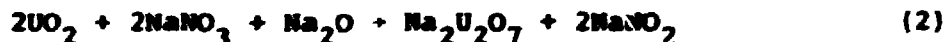
In two cases "the molten salt" cylinder was sectioned after solidification of the molten salt. A small amount of porosity was observed. It was estimated, however, that less than 2% of the fission gas was retained in the salt. Thus the gas collecting efficiency is believed to be better than 98%.

3. OXIDATION REACTIONS IN MOLTEN SALT MIXTURES

According to Ref. 9 irradiated UO_2 (and PuO_2) is oxidized in molten NaNO_3 :



This oxidation was reported to occur within 30 min. at 400°C . During the conversion of UO_2 to $\text{Na}_2\text{U}_2\text{O}_7$ the fission gases were set free quantitatively. Furthermore, it was reported that nitrous vapors could be avoided by addition of an alkaline component to the melt:



It was observed that the oxidation rate was virtually zero if the molten nitrate contained 5% nitrite. In order to avoid a very large ratio of salt to UO_2 some Na_2O_2 was added so that the formation of NaNO_2 according to eq(2) was minimized. NaOH was added to avoid nitrous vapors, NO and NO_2 . If the stoichiometric amount of Na_2O_2 is added, the overall reaction was assumed to be:



From this it was thought that the addition of NaOH might not be necessary, but so it was.

It was found that a mixture of

55 g NaNO_3

6 g NaOH

4.5 g Na_2O_2

gave a quantitative conversion of 15 g UO_2 in 4 h. The evolution of reactive nitrous fumes was avoided but N_2 and N_2O were formed. It was also tried to use a melt consisting of 30 g NaOH and 20 g Na_2O_2 , but only 3 g out of 15 g UO_2 was oxidized after 10 h.

Consequently, the above mentioned composition of NaNO_3 , NaOH and Na_2O_2 was fixed. Table 1 gives the amount of the gases which were set free by oxidation of unirradiated as well as irradiated UO_2 . It appears that the irradiated samples give about twice the amount of N_2 and O_2 and about 20 times the amount of N_2O than the unirradiated samples.

4. CALCULATION OF FISSION GAS GENERATION

4.1 Principle

Table 2 gives the cumulative fission yield of Kr and Xe isotopes originating from thermal neutron induced fission of U235, Pu239 and Pu241 together with the half lives of the unstable ones and the thermal neutron capture cross sections, as well as the resonance capture cross sections (Ref. 10 and 11).

If neither decay, nor neutron capture occurred, the calculation of the generated amount of a fission gas isotope i, $\text{FGG}(i)$ (in cm^3 (0°C, 1 ata)/g fuel) was easily done by means of

$$\text{FGG}(i) = 8.30 \cdot 10^{-3} (Y(i, \text{U235}) F(\text{U235}) + Y(i, \text{Pu239}) F(\text{Pu239}) + Y(i, \text{Pu241}) F(\text{Pu241})) \quad (4)$$

$Y(i, U235)$, $Y(i, Pu239)$ and $Y(i, Pu241)$ is the fission yield of the isotope, i , in % of U235 Pu239 and Pu241 fissions respectively, and $F(U235)$, $F(Pu239)$ and $F(Pu241)$ are the fission contributions from U235, Pu239 and Pu241 in %FIMA (% fission of initial metal atoms).

4.2 Kr Features

From table 2 it appears that Kr83 has a high neutron capture cross section, so it is expected that part of the generated Kr83 is reacting to Kr84. This isotope, however, has a quite small cross section. Consequently, the sum of Kr83 and Kr84 can be found, although the generated Kr83 and Kr84 cannot be calculated separately.

Because of decay the amount of Kr85 cannot be found directly. The Kr85 neutron capture cross section is fairly low implying that no significant amount of Kr85 reacts to give Kr86. The stable Kr86 has a very low cross section. Hence, the Kr86 generation is given directly by (4). If then the Kr85/Kr86 ratio is measured the amount of Kr85 can be found too.

4.3 Xe Features

Xe131 has a high neutron capture cross section, and Xe132 has a very low one, so the sum of Xe131 + Xe132 can be calculated.

The relatively short half life of Xe133 is the reason why it usually is not observed in fission gas. Consequently, the only question regarding Xe133 is whether the formation of Xe134 from Xe133 capturing neutrons can be neglected. Due to its short half life the concentration of Xe133 will always be quite low. Hence, it is assumed that the formation of Xe134 from Xe133 is insignificant and so the calculation of the Xe134 is simple.

Besides a short half life, Xe135 has an extremely high neutron capture cross section. The degree of Xe135 to Xe136 conversion must be very dependent of the neutron flux level and the way of

operating the reactor, i.e. whether it was on steady power for few long periods or had a large number of sort time shut downs.

Anyway the quantity of $Xe135$ converted to $Xe136$ cannot be calculated in a simple manner, unless the fission gas Xe isotope composition is known. If so, the $Xe136$ generation can be calculated from the measured ratio of $(Xe131 + Xe132)/Xe136$.

4.4 Average Fission Yields

Instead of calculating the fission gas generation from (4) and the measured isotope ratios in each single case, the average fission yield, $\bar{Y}(i)$, for isotope i , can be calculated for a selected number of burn-up levels:

$$\bar{Y}(i) = \frac{\bar{Y}(i, U235) \cdot F(U235) + Y(i, Pu239) \cdot F(Pu239) + Y(i, Pu241) \cdot F(Pu241)}{BU} \quad (5)$$

using the same notation as in (4) and BU is the total burn-up.

From (5) the fission yields for all Kr and Xe isotope (or pairs of isotopes) can be calculated except of Kr85 and Xe136 which can be calculated according to:

$$\bar{Y}(Kr85) = \frac{Kr85}{Kr86} \cdot \bar{Y}(Kr86) \quad (6)$$

and

$$\bar{Y}(Xe136) = \frac{Xe136}{Xe131+Xe132} \bar{Y}(Xe131+Xe132) \quad (7)$$

The total average fission gas yield \bar{Y} can now be found by summation of the individual isotope average yields:

$$\bar{Y} = \sum \bar{Y}(i) \quad (8)$$

From the average fission gas yield \bar{Y} the gas generated, FGG (in cm^3 ($0^\circ C$, 1 ata)/g fuel) can be calculated:

$$FGG = 8.30 \cdot 10^{-3} \cdot \bar{Y} \cdot BU \quad (9)$$

5. EXAMPLE OF RESULTS

Some of the results obtained in the RISØ Fission Gas Project by means of the method described above are presented in this section.

Table 3 gives the burn-up distribution on U235, Pu239 and Pu241 for 7 burn-up levels found from the isotopic analysis. Further, the fission gas yields calculated as outlined above are given in Table 3.

The ration $\text{Kr85}/\text{Kr86}$, which is needed in equation (6) was found to be 0.096 ± 0.002 independent of burn-up. The ratio, $\text{Xe136}/(\text{Xe131} + \text{Xe132})$, needed in equation (7) is plotted as a function of burn-up in Fig. 2. The correlation turns out to be linear within the uncertainties of the measurements.

Fig. 3 gives the calculated gas generation profile and the measured axial gas retention profile for a pin tested in the RISØ Fission Gas Project. The calculated gas generation for the pin was 381 cm^3 and the measured generation was 832 cm^3 (i.e. the area beneath the measured curve in Fig. 3 plus the release measured by puncturing) giving a relative difference of 6%.

6. ACCURACY

The overall accuracy of the measurement of the amount of retained gas is estimated to 5% (1 σ), and the accuracy of the calculation of fission gas generated is estimated to 3% (1 σ).

7. CONCLUSION

A new simple technique for measuring retained gas in irradiated fuel has been developed. The method is based on oxidation of the fuel in molten alkaline NaNO_3 .

A new method for calculation of fission gas generation has been established. The method uses the measured burn-up distribution and the measured fission gas isotopic ratios for the relevant fuel samples.

Taking 18 samples from one fuel pin the calculated and measured amount of gas for the pin as a whole agreed within 6%.

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Table 1. The amount of gases evolved per g UO_2 by oxidation of 15-20 g UO_2 in a molten mixture of 55 g NaNO_3 , 6 g and 4.5 g Na_2O_2 .

	cm^3 gas (0°C , 1 atm) per g UO_2			
	N_2	N_2O	O_2	Kr+Xe
Unirradiated UO_2 5 samples	1.03-1.73 Average 1.27	0.00-0.08 Average 0.03	0.00-2.12 Average 0.62	-
Irradiated UO_2 28 samples	2.08-3.11 Average 2.60	0.12-1.23 Average 0.55	0.00-5.21 Average 1.71	0.50-0.91

Table 2. Cumulative fission yield, half life (Ref. 10) and neutron capture cross section (Ref. 11) for the Kr and Xe isotopes relevant to fission gas formed in thermal reactor fuel.

Isotope	Fission yield (in %) in case of thermal neutron induced fission of			Half life	Neutron capture cross sections	
	U235	Pu 239	Pu241		Thermal b	Resonance b
Kr 83	0.5307	0.2948	0.2038	Stable	200	230
Kr 84	0.9861	0.4781	0.3523	Stable	0.13	2.7
Kr 85	0.2883	0.1302	0.0863	10.73 y	1.66	1.8
Kr 86	1.9511	0.7576	0.6098	Stable	0.06	0.03
Xe 131	2.8352	3.7450	3.1178	Stable	90	870
Xe 132	4.2173	5.2746	4.6251	Stable	0.36	0.8
Xe 133	6.7705	6.9729	6.6729	5.29 d	190	-
Xe 134	7.6807	7.4475	8.0313	Stable	0.25	0.3
Xe 135	6.6334	7.4665	7.0838	9.17 h	$2.65 \cdot 10^6$	$7.6 \cdot 10^3$
Xe 136	6.2730	6.6267	7.2009	Stable	0.16	-

Table 3. Calculated average fission yields for the Kr and Xe isotopes (or pairs of isotopes) observed in retained gas, the total Kr, the total Xe and the sum Kr+Xe fission yields at 7 different burnup levels for IFA 148 fuel.

Burnup % FIMA	Burnup contribution (% FIMA) from			Average fission yields in % of total fissioned atoms									Measured
				Kr 83+84	Kr 86	Kr ¹⁾ 85	Total Kr	Xe 131+132	Xe 134	Xe ²⁾ 136	Total Xe	Total Xe+Kr	Xe 136 Xe131+ Xe 132
	U235	Pu239	Pu241										
2.00	1.80	0.18	0.02	1.440	1.830	0.176	3.45	7.236	7.663	8.937	23.8	27.3	1.23
2.50	2.20	0.28	0.02	1.426	1.807	0.173	3.41	7.278	7.657	9.250	24.2	27.6	1.27
3.00	2.61	0.37	0.02	1.419	1.795	0.172	3.39	7.300	7.654	9.570	24.5	27.9	1.31
3.50	2.99	0.48	0.03	1.407	1.776	0.170	3.35	7.328	7.652	9.900	24.9	28.2	1.35
4.00	3.32	0.63	0.05	1.388	1.746	0.168	3.30	7.371	7.648	10.297	25.3	28.6	1.40
4.50	3.60	0.82	0.08	1.364	1.710	0.164	3.24	7.423	7.644	10.711	25.8	29.0	1.44
4.70	3.71	0.90	0.09	1.356	1.697	0.163	3.22	7.442	7.642	10.895	26.0	29.2	1.46

1) $\bar{Y}(\text{Kr}85) = 0.096 \bar{Y}(\text{Kr}86)$, valid on the date of reactor discharge, 26th of August 1979.

2) $\bar{Y}(\text{Xe}136) = \frac{\text{Xe}136}{\text{Xe}131 + \text{Xe}132} \bar{Y}(\text{Xe}131 + \text{Xe}132)$. The ratio $\frac{\text{Xe}136}{\text{Xe}131 + \text{Xe}132}$ given in the last column was taken from the experimental results shown in Fig.2.

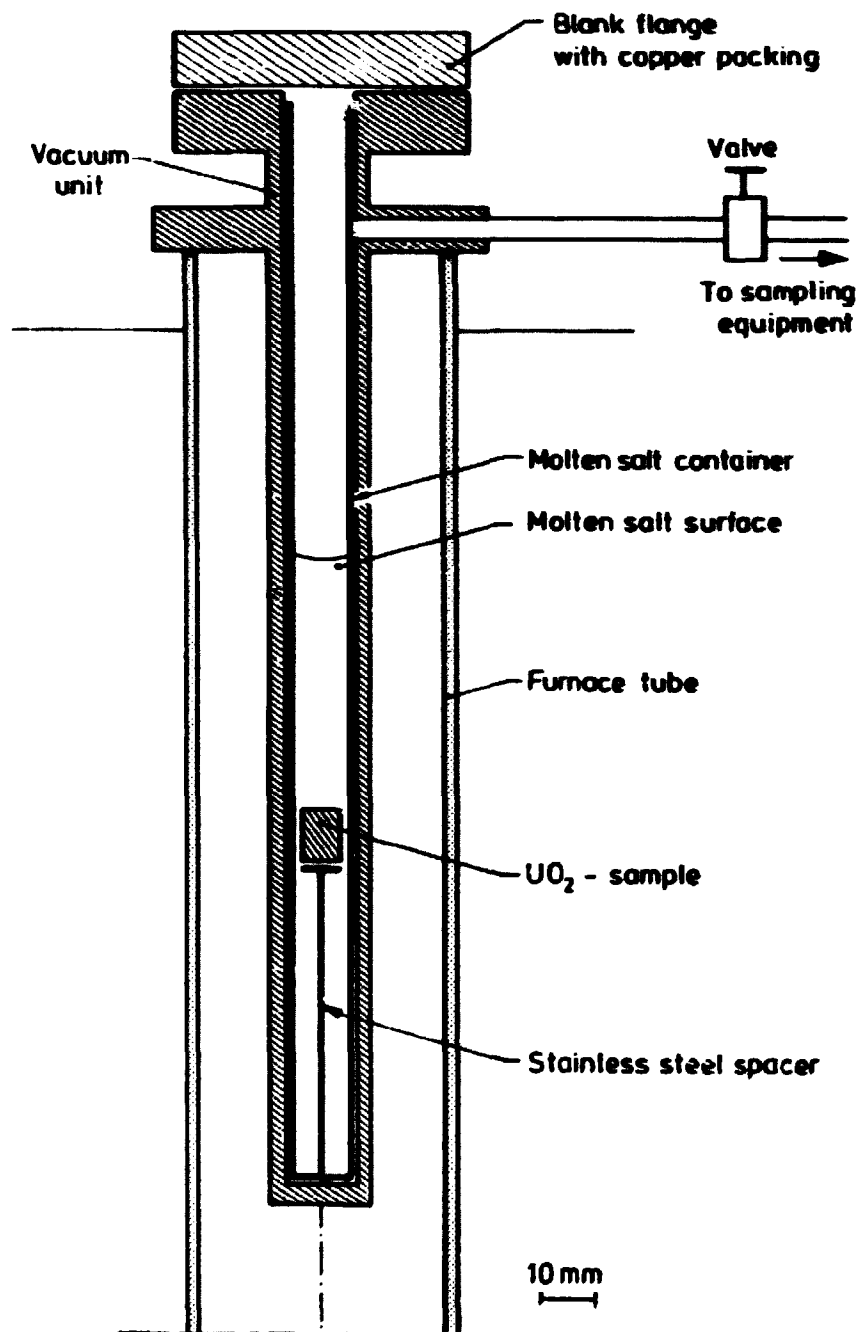


Fig. 1. Sketch of equipment used for oxidizing fuel samples in molten nitrates.

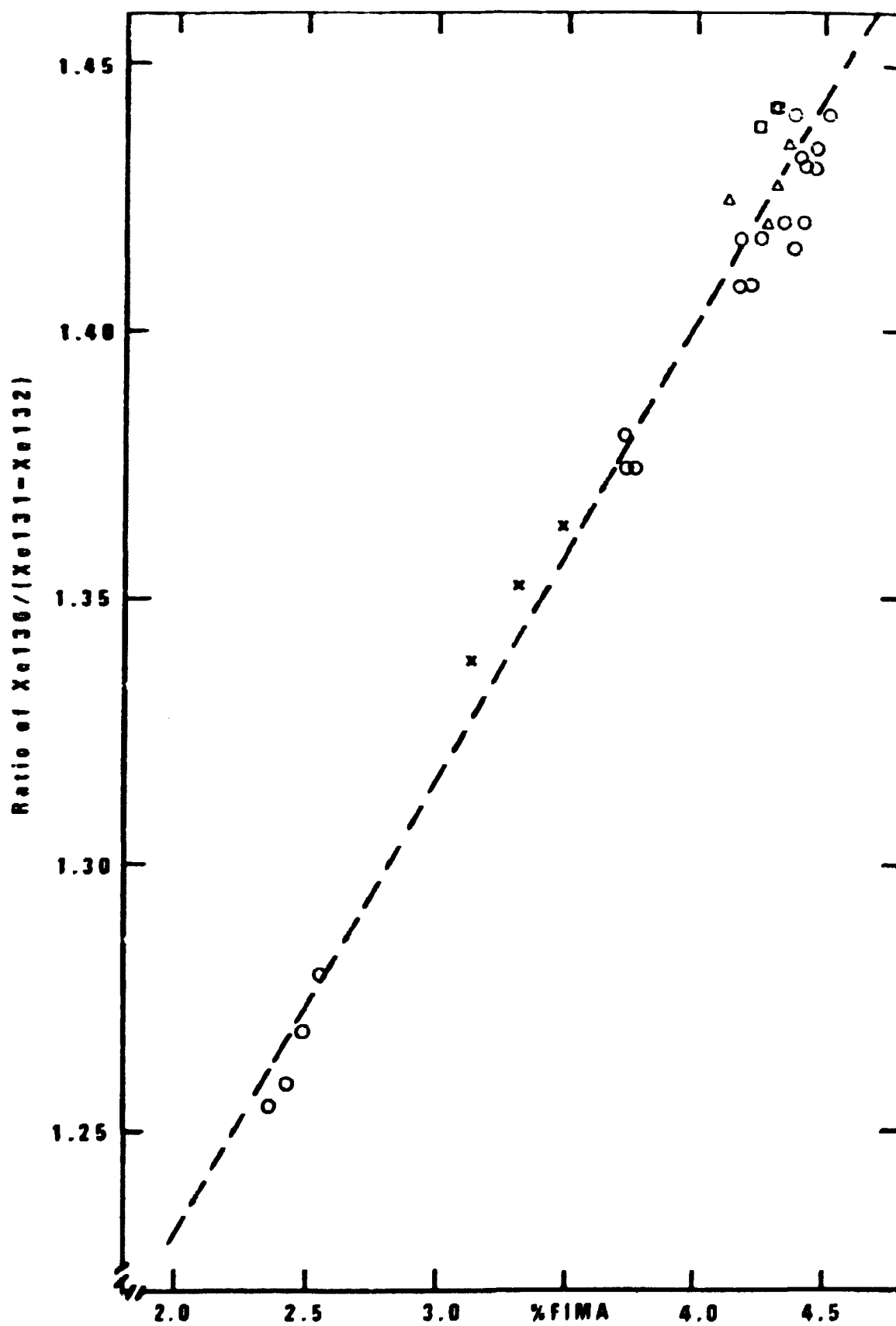


Fig. 2. The ratio of Xe136/(Xe131+Xe132) as a function of burn-up. Signatures refer to different pins in the assembly.

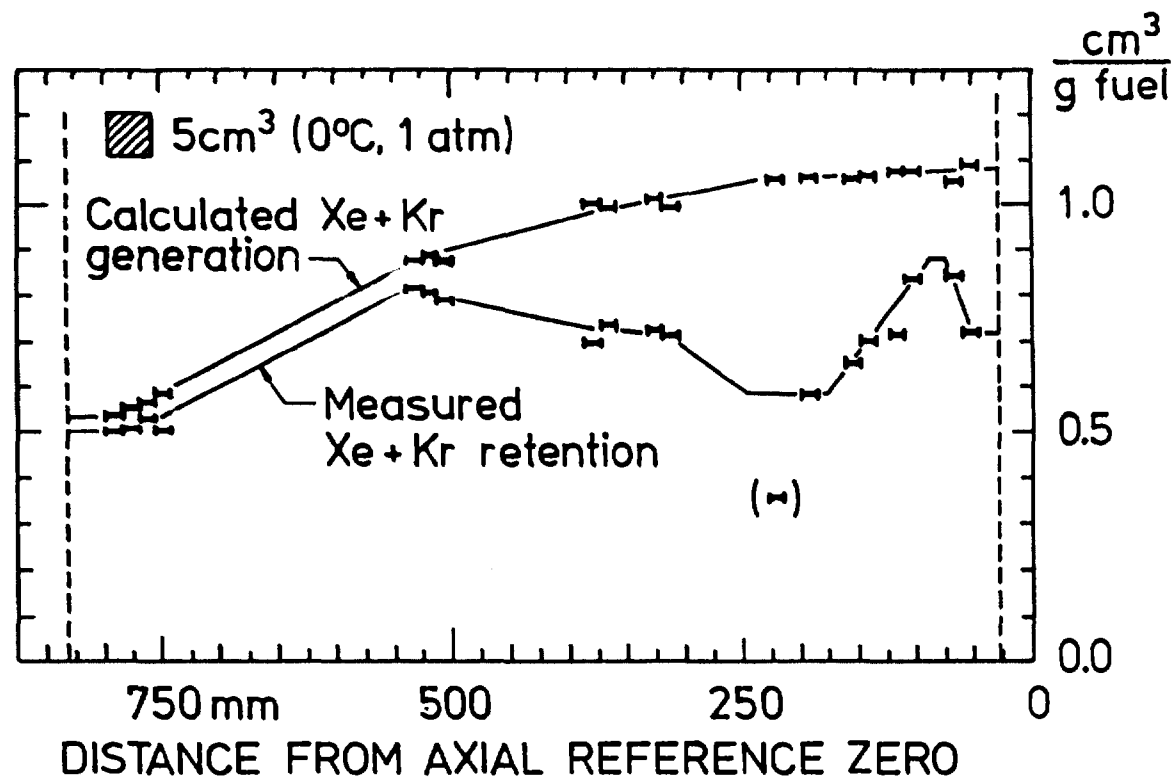


Fig. 3. Calculated gas generation and measured gas retention profile for a pin tested in the RISØ Fission Gas Project (from ref. 12).

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